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(54) **New textile materials based on polyolefins**

(57) Textile materials are made of compositions comprising a homogeneous mixture of 1 to 99% of one or several polyolefins and 99 to 1% of one or several polyetheresteramides.

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SPECIFICATION

New textile materials based on polyolefins

The present invention concerns textile materials based on new polyolefin-based compositions.

The polyolefins (polyethylene, polypropylene, etc.) are advantageously used in a wide range of applications. It is, however, known that said polyolefins are not completely satisfactory for use in textiles requiring a dyeing or tinctorial affinity or antistatic properties, for example.

Numerous methods have been proposed for dyeing polypropylene. Methods requiring the addition of epoxy resins, or acrylic copolymers or further the modification of the surface state by crown effect, etc. have among others been proposed. However, these proposed methods have remained at the level of fundamental research, and have not been practically applied; this indicates their small industrial worth.

Only mass coloration, by organic or mineral pigments, has been subject to an industrial application; this last method has however numerous drawbacks including the necessity of treating large quantities in order to obtain uniform coloration.

The present invention allows the above drawback to be overcome. Indeed, it allows obtention of polyolefin-based compositions capable of being used advantageously as textile materials and thus widens the range of polyolefin textile applications; especially it allows the obtention of polyolefin-based products having various colorations and improved anti-static properties.

The present invention concerns a textile material formed of a composition of a homogeneous mixture of one or several polyolefins and one or several polyester-amides, the said mixture being formed of 1 to 99% by weight of polyolefin and from 99 to 1% by weight of polyetheresteramide.

By polyetheresteramides are meant not only statistic polyetheramides (i.e. formed by random chaining of various monomer constituents) but also sequenced polyetheresteramides (i.e. formed by blocks having a certain chain length) as well as thir various constituents.

The polyetheresteramides are, as is well known, the product of copolycondensing polyamide blocks having reactive extremities with polyether blocks having reactive extremeties, such as, among others:

- polyamide blocks having dicarboxylic chain-ends with either α,ω-di-hydroxyl polyoxyalkylene or polyetherdiol blocks or polyetherdiamine blocks (by cyanoethylation and hydrogenation of polyether-diol):
- polyamide blocks having diamino chain-ends with polyether blocks having carboxylic chain-ends.

Such products are described in French patents 74-18913 and 77-26678, the content of which must be taken into account with the present description.

According to one embodiment of the invention, the polyamide blocks of polyetheresteramides are formed preferably from 6, 6.6, 6.12, 11 or 12 polyamide (PA-6, PA-6.6, PA-6.12, PA-12) or copolymers resulting from the polycondensation of their monomers.

Preferably, the molecular weight of these polyamide blocks is comprised between 500 and 10,000 and more especially between 1,000 and 5,000.

According to another embodiment of the invention, the polyether blocks comprise polytetramethylene glycol (PTMG) polypropylene glycol (PPG) and preferably polyethylene glycol (PEG).

Preferably, the molecular weight of the polyethers is comprised between 150 and 5,000 and more especially between 400 and 3,000.

According to a further embodiment of the invention, the previously mentioned polyetheresteramide is formed of 5 to 80%, and more especially from 30 to 60%, polyether and from 95 to 20% and preferably from 70 to 40% polyamide.

According to one way of realisation of the invention, the polyolefin consists of polypropylene (PP), polyethylene (PE), their mixtures or copolymers.

Preferably, the said mixture is formed of 75 to 99% polyolefin and 25 to 1% polyetheresteramide.

Of course, the said compositions can contain standard additives such as anti-UV, heat or light stabilizers, optical azurers, etc.

The process of obtention of these compositions consists in using the mixture of these two raw materials in powderous or granular form, drying and treating the mixture obtained in an extruder, for example, mono-screw or double-screw extruders or Buss type mixing apparatus provided with a nozzle. The rods obtained are granulated and these granules used to feed the textile spinning apparatus. It is also possible to extrude directly the textile fibres by treating the above-mentioned mixture in a suitable apparatus.

The present invention also concerns tectile materials obtained from these compositions and subsidiarily dyed textile products obtained from these compositions.

Other advantages and aims of the present invention will appear from the following description and examples given by way of non-limitative examples.

Examples 1-2

Operating occurs in a Barmag type extruding device such as used in spinning mills in order to obtain through the intermediary of a 250 brins nozzle threads of 12 d.tex. per brin.

In this extruder is treated a mixture formed of 3020 SN3 grade homopolymer propylene sold by the Company ATO CHIMIE whose melting index (measured at 230°C and under a load of 5 kg) is 8, and of a

polyetheresteramide formed of 50% PA-6 of a molecular weight equal to 1500 and of 50% PEG of a molecular weight equal to 1500.

The ponderal polyolefin/polyetheresteramide ratios in the compositions according to these examples 1 and 2 are, respectively, 95/5 and 90/10.

From the 12 d.tex threads obtained, is woven a knitted fabric that is dyed under the following conditions:

- dewaxing using an aqueous solution containing:

· Sunaptol MB® ..... 2 g/ℓ
· Galoran TSN®8 ..... 4 g/ℓ
· Trisodic phosphate ..... 2 g/ℓ

during 1 hour at 90°C,

- hot rinse then cold rinse,
- dying in a pH=5 hydroacetic solution containing:

· Dimacide blue AJL 3%
· Sunaptol LT® ..... 1 g/ℓ
· 80% acid acetic ..... qsp 100%

Dying is carried out by immersion of the knitted fabric in the said solution at 40°C, increasing the temperature to 100°C in one hour, maintaining at said temperature during 1 hour, and then cooling to 70°C.
- rinsing.

The dye obtained is a pastel shade (light) or dark according to whether a proportion of 5 or 100% polyetheresteramide is used.

The results obtained are shown in Table 1.

Examples 3 and 4

Operating is carried out according to the method described in Examples 1 and 2, and with the same constituents as those used in the same proportions while replacing, however, PA-6 by PA-12.

The physical properties determined on a knitted fabric obtained from 12 d.tex threads obtained on a knitted fabric dyed according to the method mentioned herein-above are listed in Table 1.

Example 5

By way of sample test, operating is carried out according to the method of the above-mentioned examples, while only treating polypropylene.

The dying treatments indicated herein-above is applied to a knitted fabric formed of the obtained 12 d.tex threads. It is noted that no "hooking" of the dyeing occurs (cf. Table 1).

TABLE I

Tinctorial affinity

	1	*2*	*3*	*4*	*5*
· Coloration	pastel	dark	pastel	dark	NONE
· Resistance to dry friction	5	5	5	5	
· Resistance to friction in the presence of solvent	5	5	5	5	
· Resistance to light standard NF G07067	4	5	4	5	

The analysis of the results indicated in Table 1 shows:

. it is possible to dye the polypropylene according to the technique used for the polyamides due to the addition to the polypropylene of the copolyetheresteramide, even if these copolyetheresteramides are used in weak proportions;

- it is possible to confer on the polypropylene a durable and solid dye which is resistant to various mechanical treatments and also to light action;

- resistance to friction is excellent for the textile materials according to the invention.

The measurements indicated in Table 1 were carried out under the following conditions:

- resistance to light:
by exposition to a Xenon ray arc lamp according to standard NFG 07067 which determines the resistance of the dyes on all kinds of textiles and to all their transformation stages. It consists in exposing a sample of textile of at least 10 × 45 mm to the light of an Xenon arc lamp in the conditions specified next to a range of blue standards, and then to appreciate visually the comparison of the degradation of the sample with that of the standard. Each sampe has 3 exposition zones corresponding to durations of 1, 4 and 8 days. The result is expressed by an index (cotation) comprised between 1 (very weak) and 7 (excellent).

- resistance to friction:
the resistance of the dyeing to dry friction and to friction in the presence of organic solvents are totally different. Standard NFG07016 allows determining both the resistance to friction of the dyeing on any kind of textile and, furthermore, to the running of said dyeing into another textile during friction while Standard NF G 07066 describes a method to determine the resistance of dyes on textiles of all natures and at all stages of transformation, to friction action in the presence of organic solvents (most often perchlorethylene) such as that used for cleaning by buffing.

- In these two cases, numbering goes from 1 (very weak) to 5 (excellent).

Examples 6 to 9

Similar results are obtained with the following colours:

- S3BL bordeaux double 3%
on compositions identical to those of Examples 2 to 5 respectively.

Operating occurs according to the method described in Examples 1 to 5. The results obtained are listed in Table II.

Furthermore, identical tests carried out with 3% SPLL Black give results equal to 6 for all the measurements taken.

Table II furthermore, shows that the antistatic properties are improved for knitted fabrics obtained from compositions according to Examples 1 to 4 with respect to those of knitted fabrics formed from the polyolefin of Example 5.

Antistatic measures are carried out on knitted fabrics constituted of fibres obtained from compositions according to Examples 1 to 9. The practical appreciation test of antistatic power consists in developing by friction electrostatic charges, at conditions that are always identical and determining the thus created charge. These conditions consist in operating on knitted fabrics previously degreased and perfectly conditioned, with the help of an abrasimeter known in the trade under the name Peter abrasimeter comprising a metallic screen used as a scraper. The number of friction is fixed at 450 and operating occurs at 25°C and at a relative humidity of 25%.

It is observed, within an experimental margin of error, that the products of Examples 1 to 7 have antistatic properties independent of their coloration, and clearly superior to those of the products of Example 5.

The antistatism is that much more marked as the polyether esteramide content is higher.

Naturally, this invention is in no way confined to the Examples and embodiments described above; many variant forms are possible for someone skilled in the art, depending on applications, and without any departure from the spirit of the invention.

In the preceding description, for convenience sake, polytetramethylene glycol, polyethylene glycol and polypropylene glycol have been referred to by their usual commercial names which, according to the official nomenclature, correspond to polyoxytetramethylene glycol, polyoxyethylene glycol and polyoxypropylene glycol.

TABLE II

	6	7	8	9
· Coloration	supported	darl	supported	dark
· Resistance to dry friction	5	6	5	6
· Resistance to friction in the presence of solvant	5	6	5	6
· Resistance to light standard NF G07067	4	5	4	5

CLAIMS

1. Textile material formed of a composition based on a mixture of one or several polyolefins and one or several polyetheresteramides, the said mixture being formed of 1 to 99% by weight polyolefin and 99 to 1% by polyetheresteramide.

2. Textile material according to claim 1, wherein the polyetheresteramides are statistic polyetheresteramides.

3. Textile material according to claim 1, wherein the polyetheresteramides consist of the products of the copolycondensation of polyamides blocks having reactive extremities with polyether blocks having reactive extremities, such as, among others:

· polyamide blocks having dicarboxylic chain-ends with either polyetherdiol blocks or polyetherdiamine sequences (by cyanoethylation and hydrogenation of the polyetherdiol);

· polyamide blocks having diamino chain ends with polyethers blocks having carboxylic chain ends.

4. Textile material according to claims 1 to 3, wherein the polyamide blocks of the polyetheresteramides are formed of polyamides belonging to the group formed by 6, 11, 6.6, 6.12 or 12 polyamides (PA-6, PA-11, PA-6.6, PA-6.12, P1-12) or copolyamide resulting from the copolycondensation of their monomers.

5. Textile material according to claim 4, wherein the molecular weight of polyamide blocks is comprised between 500 and 10 000.

6. Textile material according to Claim 5, wherein said molecular weight is comprised between 1000 and 5000.

7. Textile material according to Claim 1 to 3, wherein the polyether blocks consist of one of the compounds belonging to the group formed of polyoxytetramethylene glycol (PTMG), polyoxypropylene glycol (PPG) or polyoxyethylene glycol (PEG).

8. Textile material according to Claim 7, wherein the molecular weight of the polyethers is comprised between 150 and 5000.

9. Textile material according to Claim 8, wherein the molecular weight is comprised between 400 and 3000.

10. Textile material according to any one of claims 1 to 9, wherein the said polyetheresteramide is formed of 5 to 80% polyether and 95 to 20% polyamide.

11. Textile material according to Claim 10, wherein the said polyetheresteramide is formed of 30 to 60% polyether and 70 to 40% polyamide.

12. Textile material according to any one of Claims 1 to 11, wherein the polyolefin consists of polypropylene (PP) or Polyethylene (PE) or their mixtures or copolymers.

13. Textile material according to any one of Claims 1 to 12, wherein the said mixture is formed of 75 to 99% polyolefin and 25 to 1% polyether esteramide.

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